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DEVELOPMENT OF TECHNIQUES FOR PREPARING HOMOGENEOUS SINGLE CRYSTALS OF LEAD TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

J.W. Moody, et al

Battelle Memorial Institute
Columbus, Ohio

15 January 1966

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EIGHTEENTH QUARTERLY PROGRESS REPORT

on

DEVELOPMENT OF TECHNIQUES FOR PREPARING HOMOGENEOUS SINGLE CRYSTALS OF LEAD TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

to

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY

January 15, 1966

by

J. W. Moody, J. F. Miller, R. C. Himes,
and H. L. Goering

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October 15, 1965, to January 15, 1966

BATTELLE MEMORIAL INSTITUTE
Columbus Laboratories
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March 11, 1966

Dr. A. J. Strauss
Assistant Group Leader
Division 8, Group 83
Lincoln Laboratory
Massachusetts Institute of
Technology
Lexington, Massachusetts 02173

Dear Dr. Strauss:

Enclosed are ten copies of the Eighteenth Quarterly Progress Report on your project "Development of Techniques for Preparing Homogeneous Single Crystals of Lead Telluride, Lead Selenide, and Lead Sulfide". This report covers the period October 15, 1965, through January 15, 1966.

In accord with our recent verbal agreement, the experimental program will be shifted to investigation of techniques for preparing PbTe-SnTe alloy crystals.

Your comments and suggestions concerning this report and the progress of the experimental program will be welcomed.

Sincerely yours,

J. F. Miller

J. F. Miller, Associate Chief
Physical Chemistry Division

JFM:mld
Enc. (10)

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DEVELOPMENT OF TECHNIQUES FOR PREPARING HOMOGENEOUS SINGLE CRYSTALS OF LEAD TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

by

J. W. Moody, J. F. Miller, R. C. Himes,
and H. L. Goering

INTRODUCTION

This Eighteenth Quarterly Progress Report on the project is for the period from October 15, 1965, to January 15, 1966. Experimental work done in this period has been concerned primarily with investigation of the effects of mercury doping on the electrical properties of PbTe.

Accepted for the Air Force
Franklin C. Hudson
Chief, Lincoln Laboratory Office

SUMMARY

Investigation of the distribution of platinum and mercury in PbTe crystals by emission spectrographic analysis indicates that platinum is rejected from the freezing solid and tends to be concentrated in the last-to-freeze portions of the crystal. Mercury concentrations are found to be higher in the first-to-freeze portions of the crystals, but mean concentrations are low, indicating that mercury is evolved into the vapor phase of the system.

The measured electrical properties of the mercury-doped PbTe crystals were not significantly different from those of undoped PbTe prepared and treated under similar conditions; thus, the role of mercury as a dopant in PbTe was not made apparent.

Experimental investigation of techniques for the preparation of crystals of PbTe-SnTe alloy is being undertaken. Melt-growth, vapor-growth and heat-treatment techniques are to be considered.

EXPERIMENTAL DETAILS AND DISCUSSION

The investigation of platinum and mercury as dopants in PbTe, which was begun in the previous quarterly period, was continued. Distribution of the impurity elements in several of the as-grown crystals was determined by emission spectrographic analysis, and electrical properties of mercury-doped crystals were investigated.

The results of the spectrographic analyses are summarized in Table 1. The results indicate that platinum or a platinum-containing species may lower the melting point of the PbTe, and the element is segregated toward the tail of the crystal during growth.

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Crystal	Dopant	Approximate Fraction of Material Crystallized Ahead of Sample Location	Concentration of Dopant, ppm by weight
21321-85	Pt	0.1	200
	(1170 ppm by weight)(a)	0.6	3000
21321-90	Hg	0.1	100
	(600 ppm by weight)(a)	0.5	30
		0.9	25

(a) Concentration initially added to the charge.

The distribution of mercury, on the other hand, is seen to be similar to that of an impurity which raises the melting point of the solute, and the mercury is concentrated in the first-to-freeze portion of the crystal. However, the over-all concentration of mercury found in the samples indicates that not all of the mercury present was incorporated in the crystal. Some of the mercury was evolved into the free volume of the Bridgman capsule, and the measured distribution is not indicative of the equilibrium segregation of mercury in PbTe. Following the growth of Crystal 21321-90, which was doped by use of elemental mercury, elemental mercury was visible in the Bridgman capsule. Bridgman capsules have ruptured in subsequent attempts to grow crystals from melts doped with higher concentrations of mercury. Since the free mercury was present in the capsule, it is probable that Crystal 21321-90 contains the maximum concentration of mercury that may be introduced during growth from the melt. It is likely also that not all of the mercury added to the melts was incorporated in Crystals 19733-8 and 19733-9 (Table 2) and that mercury concentrations are significantly below those which might be deduced from melt compositions given for these crystals in Table 2. Especially is this likely for Crystal 19733-9, since the concentration of mercury was very large. Even though the mercury was introduced by adding mercury telluride, the evolution of free mercury into the vapor phase is likely to have occurred at the growth temperature.

Data on the compositions of melts utilized for growth of the three mercury-doped crystals that were studied are given in Table 2. Crystal 21321-90 was grown at 0.05 inch per hour from a melt of the congruent-melting Pb-Te composition to which was added 0.1 atomic per cent of elemental mercury. Crystals 19733-8 and 19733-9 were grown previously (Seventh Quarterly Progress Report, April 15, 1963) from melts doped with mercury telluride.

All three ingots were p-type. The Hall coefficients and resistivities of crystals from near the head of the "as-prepared" ingots are shown as a function of reciprocal temperature in Figures 1 and 2. Free carrier concentrations are high and those for Crystal 19733-8 are not "well-behaved" functions of temperature. Hole mobilities, calculated from the rate R/ρ are moderately high for the carrier concentrations prevailing in the crystals. No explanation is apparent at this time for the characteristic of the Hall coefficient for Crystal 19733-8. Recheck and further study of this is to be made if another specimen from the ingot is found to display the same characteristic.

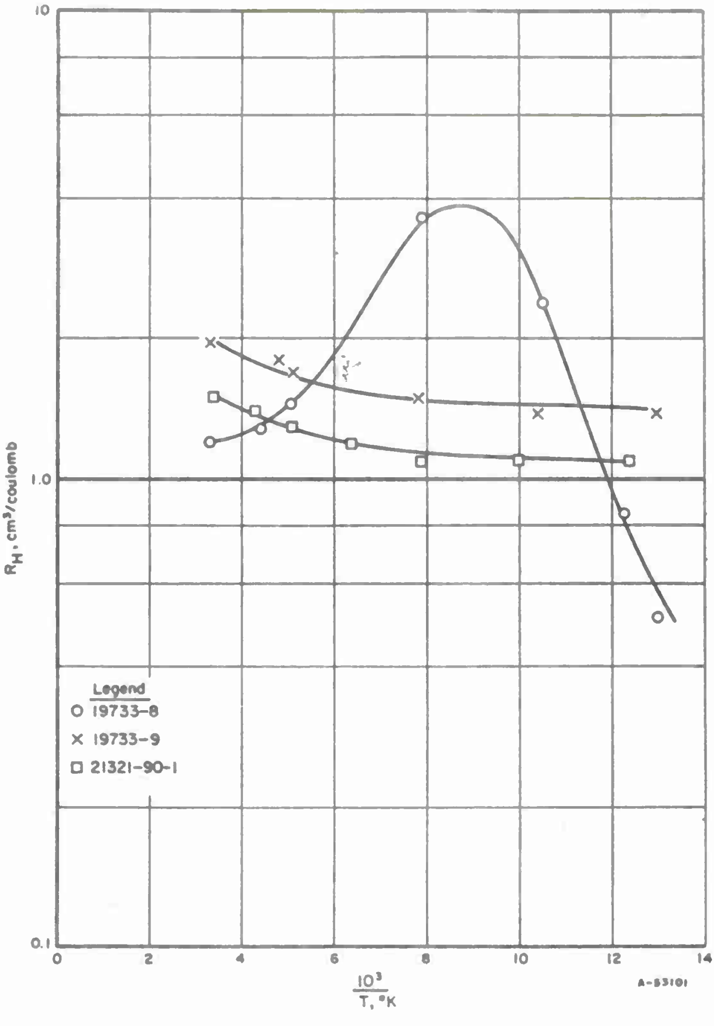

FIGURE 1. HALL COEFFICIENT AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR "AS PREPARED" MERCURY-DOPED PbTe

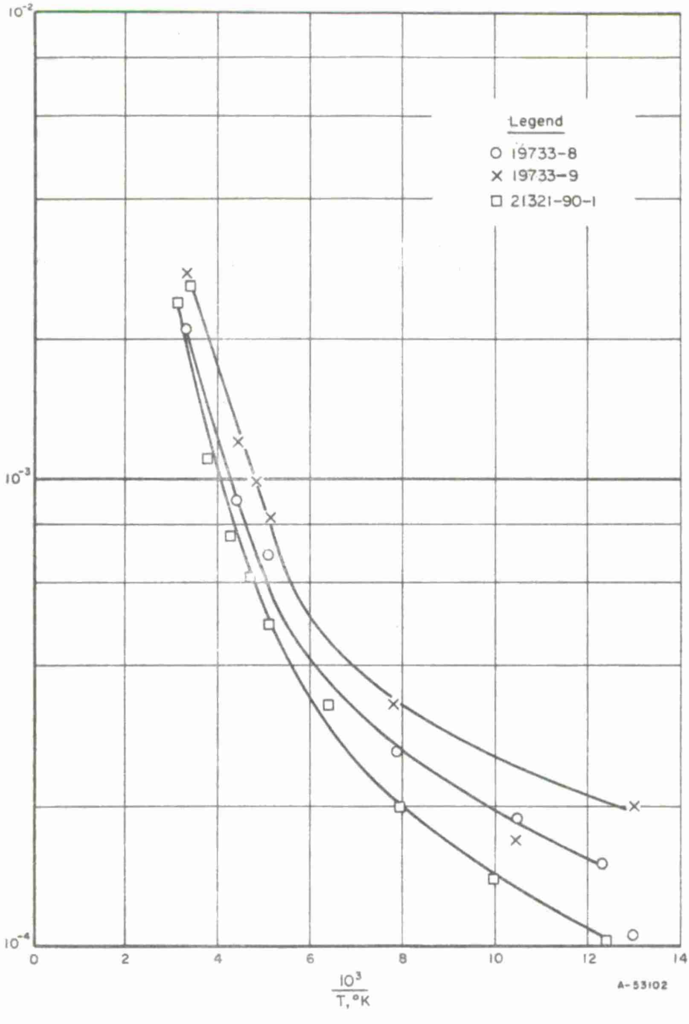

FIGURE 2. RESISTIVITY AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR "AS-PREPARED" MERCURY-DOPED PbTe

TABLE 2. SYNTHETIC COMPOSITION OF MERCURY-DOPED MELTS

Ingot	Melt Composition (atom fraction) Pb	Te	Hg	Excess Te (atomic percent) Based on Pb-Te Ratio	Based on Metal-Te Ratio
19733-8	0.4997	0.50019	0.00004	0.084	0.076
19733-9	0.49630	0.50019	0.00351	0.784	0.076
21321-90	0.49973	0.49987	0.00050	0.028	-0.072

Crystals from Ingots 19733-8 and 19733-9 were annealed in the vapor of Pb-rich PbTe stock at 855°C and program cooled. This treatment converted the crystals to n-type. Electrical properties at 77°K of the heat-treated crystals are included in Table 3. The mobilities of the crystals are neither exceptionally high nor low for the measured carrier concentrations. Electrical properties of 19733-9 are shown as a function of temperature in Figure 3. The properties appear to be "well behaved" functions of temperature and exhibit no evidence of the double-crossover behavior observed for some n-type, low-carrier-concentration crystals.

Crystals from Ingot 21321-90 have also been annealed at elevated temperatures in the vapor of Pb-rich PbTe stock. After 48 hours at anneal temperature, the crystals were quenched. All crystals were converted to n-type by the heat treatment. Their properties also are listed in Table 3. The crystals contained about 30 ppm Hg before heat treatment. Except for 21321-90-2, the crystals appear to be compensated after heat treatment. However, sufficient data on the relationship between carrier concentration and heat-treatment temperature for PbTe crystals have not been obtained to permit firm evaluation of crystals on this basis. Data presented in the previous quarterly report (dated October 15, 1965) clearly show that platinum is a donor in PbTe. The effects of mercury, on the other hand, appear to be more subtle, and the role of mercury is not clear from the experimental results obtained to date in this work.

FUTURE WORK PLANS

In accord with the recent verbal agreement, it is planned that the studies of the doping of PbTe that have been conducted in the past two quarters will be phased out and that emphasis is to be shifted to investigation of techniques for the preparation of crystals of PbTe-SnTe alloy. Experiments already underway on the purified or doped PbTe, including measurements of the electrical properties of selected vacuum-sublimed and doped crystals down to liquid helium temperature, are to be concluded.

Several approaches to preparation of the alloy crystals are to be considered: growth by melt techniques, growth by melt techniques followed by heat treatment under appropriate conditions, and growth by vapor techniques. Initially, efforts are to be concerned primarily with growth of PbTe-rich alloy crystals in which the SnTe concentration is below 20 mole per cent. However, some experiments may be conducted with SnTe, SnTe-rich alloys, and with PbSe-SnSe alloys.

Data upon which this report is based are recorded in Battelle Laboratory Record Book No. 21321, pp 89-100 and 23046, pp 1-3.

TABLE 3. EFFECT OF HEAT TREATMENT ON MERCURY-DOPED PbTe

Crystal	Anneal Temperature, °C	Method of Cooling	Hall Coefficient, cm^3/coulomb	Properties (at 77°K) After Anneal: Resistivity, ohm-cm	Properties (at 77°K) After Anneal: Mobility, cm^2/volt-sec	Carrier Concentration, cm^{-3}
19733-8	855	Program[a]	-110	5.5×10^{-3}	2.0×10^{4}	5.7×10^{16}
19733-9	855	Program	-45	1.2×10^{-3}	3.3×10^{4}	1.4×10^{17}
21321-90-4	850	Quench	-9.3	4.5×10^{-3}	2.1×10^{3}	6.8×10^{17}
21321-90-2	800	Quench	-2.2	8.8×10^{-5}	2.5×10^{4}	2.9×10^{18}
21321-90-1	750	Quench	-8.8	3.9×10^{-4}	2.2×10^{4}	7.2×10^{17}

(a) To 400°C for 72 hours, then 300°C for 240 hours, then to room temperature.

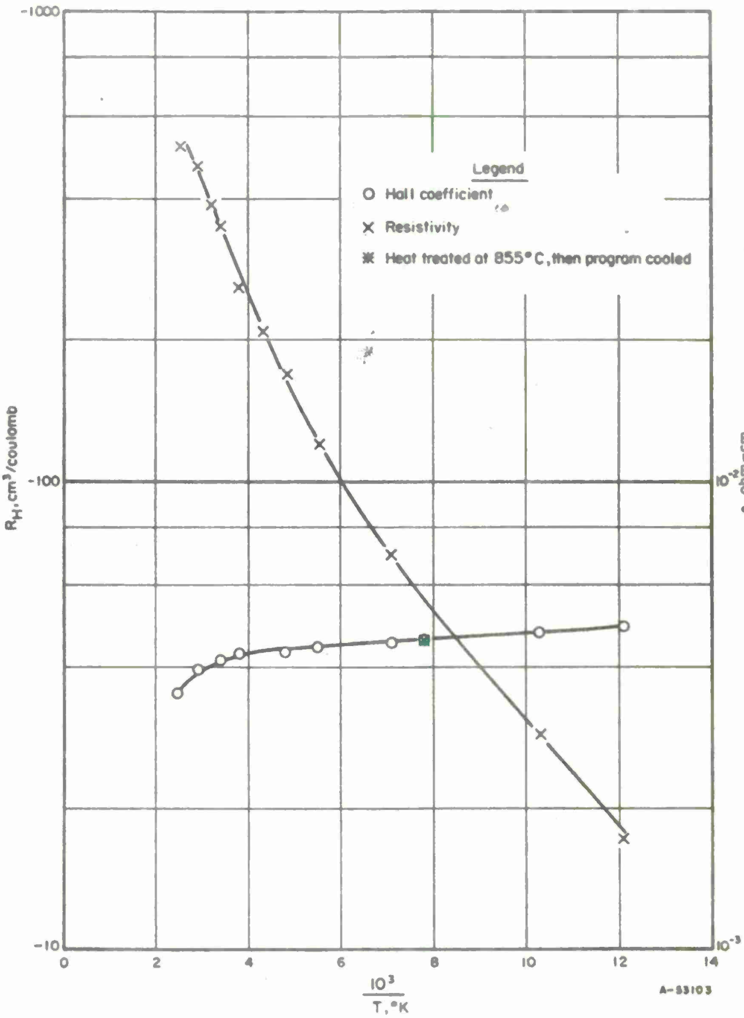

FIGURE 3. HALL COEFFICIENT AND RESISTIVITY AS FUNCTIONS OF RECIPROCAL TEMPERATURE FOR ANNEALED* MERCURY-DOPED PbTe (19733-9)

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13. ABSTRACT

Experimental work done in this period has been concerned primarily with investigation of the effects of mercury doping on the electrical properties of PbTe.

Investigation of the distribution of platinum and mercury in PbTe crystals by emission spectrographic analysis indicates that platinum is rejected from the freezing solid and tends to be concentrated in the last-to-freeze portions of the crystal. Mercury concentrations are found to be higher in the first-to-freeze portions of the crystals, but mean concentrations are low, indicating that mercury is evolved into the vapor phase of the system.

The measured electrical properties of the mercury-doped PbTe crystals were not significantly different from those of undoped PbTe prepared and treated under similar conditions; thus, the role of mercury as a dopant in PbTe was not made apparent.

Experimental investigation of techniques for the preparation of crystals of PbTe-SnTe alloy is being undertaken. Melt-growth, vapor-growth and heat-treatment techniques are to be considered.

14. KEY WORDS

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